Bicyclization of Enynes Using the Cp_2TiCl_2−Mg−BTC System: A Practical Method to Bicyclic Cyclopentenones

Zongbao Zhao, Yu Ding,* and Gang Zhao

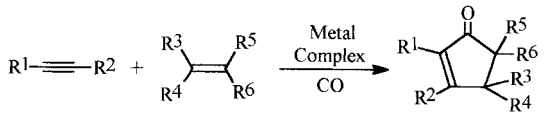
Shanghai Institute of Organic Chemistry, Academia Sinica, 354 Fenglin Lu, Shanghai 200032, People's Republic of China

Received June 5, 1998

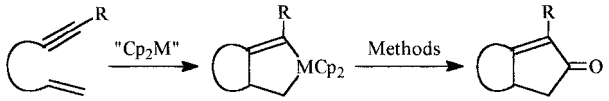
Bicyclic titanacycles **2** generated with the Cp_2TiCl_2−Mg−$P(OEt)_3$ system can be trapped with bis(trichloromethyl) carbonate (BTC) to give bicyclic cyclopentenones **3** in good yields. The titanacycle **2m** was isolated and well-identified. Bicyclization of enynes containing 1,2-disubstituted olefin by this method gave good results with excellent stereoselectivity.

In recent years, cyclization reaction of alkenes with alkynes and carbon monoxide mediated by transition-metal complexes (Scheme 1) has been paid much attention, not only with the view of methodology research, but also with that of organic synthesis. The most popular version of this reaction mediated by $Co_2(CO)_8$, known as the Pauson−Khand reaction, has become one of the most powerful and convergent methods for the construction of cyclopentenones,[1] and several fruitful modifications have made it more effective.[2] Besides cobalt complexes, many other complexes of transition metals,[3] including Fe, W, Cr, Mo, Ni, Ru, Rh, Ti, etc., have been used to mediate this important transformation with various results. Up to now, several natural products and their analogues have been synthesized by using the Pauson−Khand reaction as a key step.[4]

Scheme 1



Scheme 2[a]



[a] Method A: CO, M = Ti, Zr. Method B: R_3SiCN, then HOAc or $CuSO_4$, M = Ti.

Group IV metallocenes were also introduced to bicyclization of enynes to construct the bicyclic cyclopentenone skeleton (Scheme 2), similar to an intramolecular Pauson−Khand reaction. In previous pioneering research, Negishi and co-workers[5] used the Cp_2ZrCl_2/2*n*-BuLi system (Negishi reagent) to bicyclize enynes with CO. Buchwald and co-workers,[6] however, used $Cp_2Ti(PMe_3)_2$ or $Cp_2Ti(CO)_2$ as a metallocene equivalent[6c,7] to effect this reaction.

Most of the above methods require medium- or high-pressure CO, elevated temperature, long reaction time, and expensive and/or unstable metal complexes. Although isocyanides and trialkylsilyl cyanides have been reported to be CO equivalents in this reaction (Scheme 2, method B), the procedure is still time-consuming and tedious.[7] In a research project on the reactions mediated by low-valent titanocene species, we found that bis(trichloromethyl) carbonate (BTC), which is a stable white crystal and has been recently used in introducing a carbonyl group in organic synthesis (Scheme 3),[8] could be a useful substitute of CO and trialkylsilyl cyanides to trap the titanacycles 2 (Scheme 4). The interesting reaction provided us a simple and practical method to

* To whom correspondence should be addressed. Tel.: 86-21-64163300. Fax: 86-21-64166128. E-mail: dingyu@pub.sioc.ac.cn.

(1) For reviews, see: (a) Schore, N. E. *Org. React.* **1991**, *40*, 1. (b) Schore, N. E. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G., Wilkinson, G., Eds.; Elservier Press: New York, 1995; Vol. 12, p 703. For recent examples of this reaction, see: (c) Ahmar, M.; Locatelli, C.; Colombier, D.; Cazes, B. *Tetrahedron Lett.* **1997**, *38*, 5281. (d) Jordi, L.; Ricart, S.; Vinas, J. M.; Moretó, J. M. *Organometallics* **1997**, *16*, 2808.

(2) For effecting this reaction using dry-state adsorption techniques, see: (a) Smit, W. A.; Kireev, S. L.; Nefedov, O. M.; Tarasov, V. A. *Tetrahedron Lett.* **1989**, *30*, 4021. (b) Smit, W. A.; Gybin, A. S.; Simonyan, S. O.; Shashkov, A. S.; Tarasov, Y. T.; Strychkov, Y. T.; Kyz'mina, L. G.; Mikaelian, G. S.; Cable, R.; Swanson, E. D. *Tetrahedron Lett.* **1986**, *27*, 1241. For effecting this reaction using various additives, see: (c) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Tetrahedron Lett.* **1990**, *31*, 5289. (d) Kraft, M. E.; Scott, I. L.; Romero, R. H.; Feibelmann, S.; Vanpelt, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 7199. (e) Billington, D. C.; Helps, I. M.; Pauson, P. L.; Thomson, W.; Willison, D. *J. Organomet. Chem.* **1988**, *354*, 233. (f) Chung, Y. K.; Lee, B. Y.; Jeong, N.; Hudecek, M.; Pauson, P. L. *Organometallics* **1993**, *12*, 220. (g) Sugihara, T.; Yamada, M.; Ban, H.; Yamaguchi, M.; Kaneko, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2801. (h) Rajesh, T.; Periasamy, M. *Tetrahedron Lett.* **1998**, *39*, 117.

(3) For Fe, see: (a) Pearson, A. J.; Dubbert, R. A. *Organometallics* **1994**, *13*, 1656. (b) Knolker, H. J.; Heber, J. *Synlett* **1993**, 924. (c) Pearson, A. J.; Yao, X. *Synlett* **1997**, 1281. (d) Pearson, A. J.; Dubbert, R. A. *J. Chem. Soc., Chem. Commun.* **1991**, 202. For W, see: (e) Hoye, T. R.; Suriano, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 1154. For Cr, see: (f) Jordi, L.; Segundo, A.; Camps, F.; Ricart, S.; Moreto, J. M. *Organometallics* **1993**, *12*, 3795. For Mo, see: (g) Jeong, N.; Lee, S. J.; Lee, B. Y.; Chung, Y. K. *Tetrahedron Lett.* **1993**, *34*, 4027. For Ni, see: (h) Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 1286. (i) Tamao, K.; Kobayashi, K.; Ito, Y. *Synlett* **1992**, 539. (j) Buchwald, S. L.; Zhang, M. *J. Org. Chem.* **1996**, *61*, 4498. For Ru, Rh, Ti, see ref 18.

(4) For examples, see: (a) Jamison, T. F.; Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 5505. (b) Tormo, J.; Moyamo, A.; Pericàs, M. A.; Rieca, A. *J. Org. Chem.* **1997**, *62*, 4851. (c). Yoo, S. E.; Lee, S. H. *J. Org. Chem.* **1994**, *59*, 6968. (d) Alcaide, B.; Polanco, C.; Sierra, M. A. *Tetrahedron Lett.* **1996**, *37*, 6901.

(5) (a) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. (b) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cedarbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336.

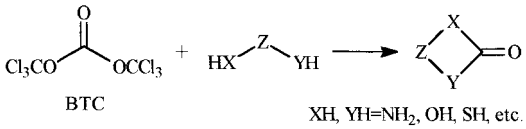
(6) (a) Beck, S. C.; Grossman, R. B.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8593. (b) Grossman, R. B.; Buchwald, S. L. *J. Org. Chem.* **1992**, *57*, 5803. (c) Hicks, F. A.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 9450. (d) Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6422.

(7) Hicks, F. A.; Berk, S. C.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 2713.

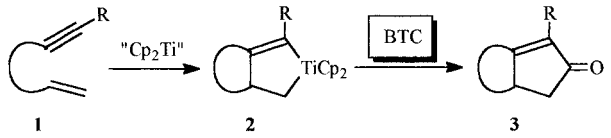
(8) For an extensive review, see: Cotarca, L.; Delogu, P.; Nardelli, A.; Sunjié, V. *Synthesis* **1996**, 553.

10.1021/jo9810718 CCC: $15.00
Published on Web 11/21/1998

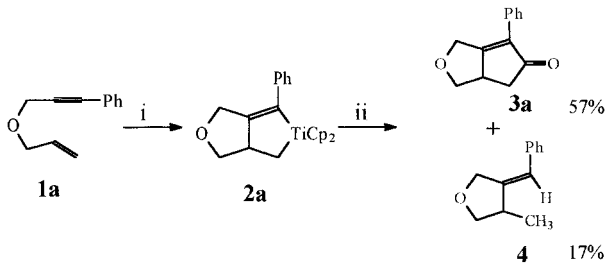
Scheme 3



Scheme 4



Scheme 5[a]



[a] Key: (i) Cp_2TiCl_2/Mg, THF, 0 °C, 6 h; (ii) 1.5 equiv of BTC, 0 °C, 2 h.

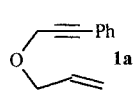
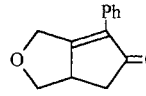
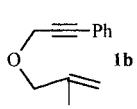
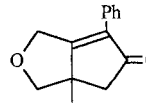
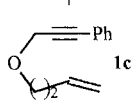
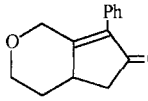
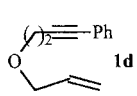
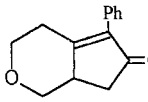
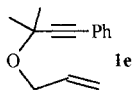
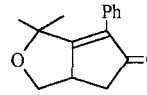
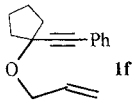
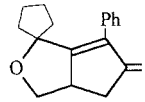
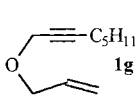
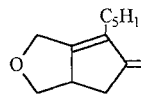
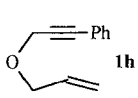
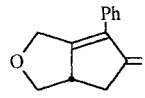
construct bicyclic cyclopentenone skeleton from the corresponding enynes with relatively stable starting material in short reaction time.[9] Here, we would like to report our results.

Results and Discussions

The titanacycles **2** were generated according to a recent published procedure.[10] Thus, a mixture of enyne **1a**, Cp_2TiCl_2, and Mg turnings activated with 1,2-dibromoethane was stirred at 0 °C for 6 h (procedure A) to form the key intermediate **2a**, which was relatively stable and could be detected on TLC (silica gel, developed with petroleum ether/ethyl acetate). If **2a** was treated with 1.5 equiv of BTC, the desired bicyclic cyclopentenone **3a** was produced as expected in 57% yield, and a byproduct **4** was formed in 17% yield (Scheme 5). Obviously, **4** can be envisioned as protonated product from **2a**. We wondered if the byproduct **4** came from the reaction of **2a** with moisture or not, but even the use of a strict Schlenk technique or introduction of MS 4 Å has been proven unsuccessful to avoid this byproduct. To improve the yield, we then tried various ligands to stabilize the intermediate **2a**. When 2 equiv of $P(OEt)_3$ was introduced,[11] the yield of **3a** increased, indeed, up to 75%. To our surprise, the byproduct **4** could still be isolated in about 17% yield. Other ligands, such as $P(OMe)_3$, PPh_3, and bis(trimethylsilyl)acetylene, gave poor results in this reaction, though they have already been used to stabilize titanocene complexes elsewhere.[12]

When we checked the role of Mg activity, we were very pleased to obtain satisfactory results using Aldrich Mg powder (procedure B) without any activation. In this case, only traces of monocyclic compounds such as **4** were detected according to TLC monitoring. Therefore, we believe that most of the monocyclic products may derive from the reaction between the titanacycles **2** and the Grignard reagent resulting from Mg turnings and 1,2-dibromoethane, though the detailed mechanism is still unknown. This hypothesis was further verified, since yields of **3a** up to 77% were achieved when the Mg turnings were separated off from the resulting mixture in the activating stage.

Table 1. Cyclopentenones from Enyne Ethers

Substrate	Product	Entry	Method[a]	Yield/%[b]
 **1a**	 **3a**	1	A	75
		2	B	82
 **1b**	 **3b**	3	A	42
		4	B	84
 **1c**	 **3c**	5	A	30
 **1d**	 **3d**	6[c]	A	39
		7[c]	B	63
 **1e**	 **3e**	8	B	54
 **1f**	 **3f**	9	A	43
		10	B	78
 **1g**	 **3g**	11	A	41
		12	B	77
 **1h**	 **3h**	13	A	45
		14	B	64

[a] All reactions were performed on a 2 mmol scale. For details, see the Experimental Section. [b] Isolated yields of products >95% purity as estimated by ^1H NMR analysis. [c] The desired product can only be obtained in the absence of $P(OEt)_3$ and thus gave lower yield.

The results summarized in Table 1 demonstrate the generality of this reaction. Six-membered ring system (**3c** and **3d**) and quaternary center (**3e** and **3f**) containing products can be formed with this technique. More interestingly, enyne **1h**, which is an optically pure substrate, gave only one isomer **3h**. Strong interaction between 6-H (δ 3.64) and 5-H (δ 3.17) in **3h** was recorded by an NOE analysis, which means a *cis* relationship of the two protons. Thus, **3h** should be the 5*S*,6*R* isomer. In this case, the newly formed chiral center was well-controlled, and the interesting stereocontrol will be useful in organic

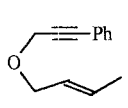
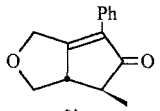
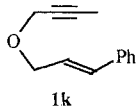
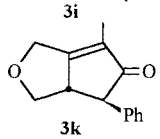
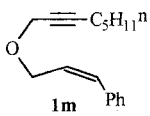
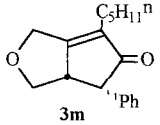
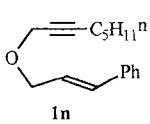
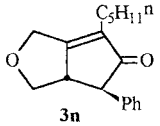
(9) Part of this work has been communicated. Zhao, Z.; Ding, Y. *J. Chem. Soc., Perkin Trans. 1* **1998**, 171.

(10) (a) Miura, K.; Funatsu, M.; Saito, H.; Ito, H.; Hosomi, A. *Tetrahedron Lett.* **1996**, *37*, 9059. (b) Pearson, D. E.; Cowan, D.; Beckler, J. D. *J. Org. Chem.* **1959**, *24*, 504.

(11) (a) Horikawa, Y.; Watanabe, M.; Fujiwara, T.; Takeda, T. *J. Am. Chem. Soc.* **1997**, *119*, 1127. (b) Takeda, T.; Shimoka, H.; Miyachi, Y.; Fujiwara, T. *Chem. Commun.* **1997**, 1055.

(12) (a) Rosenthal, U.; Ohff, A.; Michalik, M.; Görls, H.; Burlakov, V. V., Shur, V. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1193. (b) Lefeber, C.; Arndt, P.; Tillack, A.; Baumann, W.; Kenpe, R.; Burlakov, V. V.; Rosenthal, U. *Organometallics* **1995**, *14*, 3090. (c) Horikawa, Y.; Nomura, T.; Watanabe, M.; Fujiwara, T., Takeda, T. *J. Org. Chem.* **1997**, *62*, 3678.

Table 2. Cyclopentenones from Enynes Containing 1,2-Disubstituted Olefin[a]

Substrate	Product	Entry	Method	Yield/%[b]
 **1i**	 **3i**	1[c]	B	63[d]
 **1k**	 **3k**	2	A	32
 **1m**	 **3m**	3	B	74
 **1n**	 **3n**	4	B	61

[a] Only one isomer was isolated in all cases; the stereochemistry of the products was unambiguously assigned by NOE analysis. [b] Isolated yield. [c] The starting material was also recovered in about 50% yield. [d] This yield was based on the converted starting material.

synthesis. The benzyl ether group presented in enyne **1h** is tolerable to the reaction condition.

One of the major drawbacks of bicyclization of enynes mediated by group IV metallocene so far is its failure in conversions of substrates containing 1,2-disubstituted olefin.[6a] Very recently, $Cp_2Ti(CO)_2$ was found to be an alternative to cyclize this kind of enynes.[6c] However, there are still no transformation examples of enyne ethers containing 1,2-disubstituted olefin with Group IV metallocenes. Fortunately, enyne **1i** could be converted to the corresponding cyclopentenone **3i** in moderate yield with our system, and at least three other substrates were found to give good yields (Table 2), probably because the phenyl group presented in these substrates benefited the reaction. It should be noted that only one stereoisomer was isolated, and in each case the stereochemistry of the double bond was well-related with that of the product, i.e., the (*E*)-enynes producing 4,5-trans products, and vice versa, the (*Z*)-enynes giving 4,5-cis products. These outcomes showed better stereoselectivity than the related $Cp_2Ti(CO)_2$ procedure.[6c]

Bicyclic titanacyclopentenes **2** are very important intermediates in titanocene chemistry, and their analoguous titanacyclobutene complexes have been well-characterized in the literature.[13] However, to our knowledge, intermediates **2** have not been separated and identified. To see if the stereochemistry has already been established at the stage of titanacycle formation, we have tried to isolate and identify complexes **2**. Fortunately, the titanacycle **2m**, generated from enyne **1m** using the Cp_2TiCl_2–Mg system, was found to be stable in chromatography on silica gel. An NOE analysis of **2m** demonstrated the relationship between the α-H and *β*-H as shown in Scheme 6. This observation shows that the formation of titanacycles is a highly stereospecific reaction and that

Scheme 6

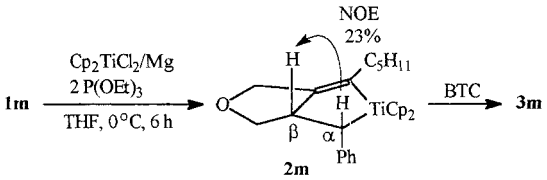
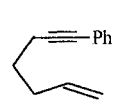
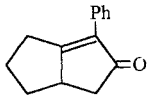
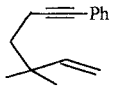
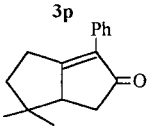
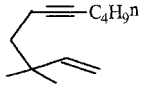
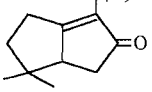
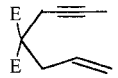
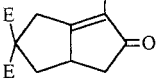
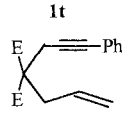
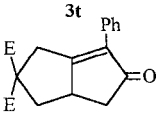
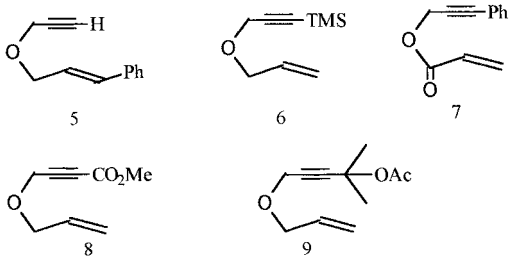


Table 3. Cyclopentenones from Oxygen-Free Enynes

Substrate	Product	Entry	Method	Yield/%[a]
 **1p**	 **3p**	1	A	42
		2	B	85
 **1q**	 **3q**	3	A	70
 **1s**	 **3s**	4	B	58
 **1t**	 **3t**	5[b]	B	82
 **1u**	 **3u**	6[b]	A	46
		7	B	65

[a] Isolated yield. [b] E = CO_2Et.

Scheme 7



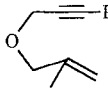
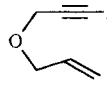
the reaction between titanacycles **2** and BTC proceeds with conservation of configuration.

Enynes without an oxygen atom within the tether also gave good results as demonstrated in Table 3. The ester groups present in enynes **1t** and **1u** did not interfere with the reaction, and the expected products were obtained in good yields.

Some other substrates listed in Scheme 7 were then chosen to study the scope of this reaction. An attempt to convert enyne **5** containing a terminal alkyne under our conditions was unsuccessful—an outcome consistent with what had been published elsewhere.[6a] Enyne **6** can be converted into the corresponding titanacycle, as judged by TLC analysis. Unfortunately, attempts to trap the latter with BTC failed to afford the desired product. It should be noted that similar difficulty in bicyclization of trimethylsilyl-containing enyne has been reported by Buchwald[6a] in the previous work. Enyne **7** containing a carbonyl group within the tether between the alkyne and

(13) (a) Ogoshi, S.; Stryker, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 3514. (b) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149.

Table 4. Trapping Titanacycles Generated from Various Methods Using BTC[a,b]

Substrate	Reaction Conditions	Yield/%[c]
	Cp_2TiCl_2/Mg, 0°C, THF, 6 h	84
	Cp_2TiCl_2/2 n-BuLi, −78 °C−0 °C, THF, 6 h	60
	Cp_2TiCl_2/Mg, 0°C, THF, 6 h	82
	Cp_2TiCl_2/2 EtMgBr, −78 °C−0 °C, THF, 3 h	52
	Cp_2TiCl_2/2 EtMgBr, 0°C, THF, 6 h	42

[a] 2 equiv of $P(OEt)_3$ was used as a ligand in all systems in order to make it more comparable. [b] 1.5 equiv of BTC was used to trap the titanacycles generated under the conditions described. [c] Isolated yields.

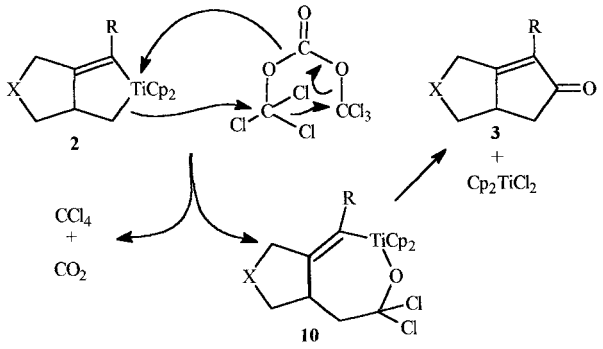
the olefin unit was converted to a complex mixture. Enynes **8** and **9** were also completely consumed with the Cp_2TiCl_2−Mg system to afford a complex mixture.

To determine the generality of BTC in this chemistry, we used BTC as a substitute for CO to react with titanacycles **2** generated from enynes **1a** and **1b** using other known methods. The desired product could be obtained when either the Cp_2TiCl_2/2EtMgCl or Cp_2TiCl_2/2*n*-BuLi system[14] was used, giving a little poorer yield than ours (Table 4), presumably because of uncertain concentration of the alkylmetal reagents and other side reactions. However, the Ti(O-*i*Pr)$_4$/2PrMgCl system[15] failed to give any bicyclic cyclopentenone.

We then studied the mechanism of reaction between the titanacycles and BTC. Since it is known that BTC can generate phosgene ($COCl_2$) in situ, we first checked the possibility of this pathway. When $COCl_2$ gas was bubbled into a THF solution of titanacycle **2a** generated by general procedure A for 5 min, **3a** could be isolated in 56% yield. Thus, it seems to be similar to the formation of main-group elements containing heterocycles mediated by zirconacene complex.[16] We observed that when BTC was introduced to the solution of titanacycles, much gas was formed immediately. The gas was proven to be CO_2 by its characteristic reaction with lime solution. Additionally, a GC analysis verified the presence of CCl_4 in the reaction mixture. We found that the yield decreased when BTC was loaded in less than 1 equiv. From the above observations, it was deduced that BTC only transferred one carbonyl group to the intermediate. Thus, the authors suggest a direct attack between the titanacycles **2** and BTC, even though BTC can in situ generate $COCl_2$ and that $COCl_2$ was proven to be able to trap the titanacycle (vide ante). The reaction might proceed through the following tentative mechanism (Scheme 8), though it is still unclear how the postulated intermediate[17] **10** transformed to the final cyclopentenone **3**. This hypothesis may account for release of CO_2 and the stereoselectivity in the reaction of 1,2-disubstituted olefin containing enynes.

According to this mechanism, Cp_2TiCl_2 was regenerated. Indeed, pure Cp_2TiCl_2 was recovered in 47% yield in a typical experiment when the reaction mixture was filtered through a short silica gel plug followed by concentration and recrystallization from chloroform. Thus, this method provided the first example of regenerating Cp_2TiCl_2 in bicyclization reactions mediated by titanocene. With the above results in hand, we then tried to transform this reaction into a catalytic one.[18] When 0.5 equiv of Cp_2TiCl_2 was used to convert **1a** into **3a** by general procedure B, the isolated yield of **3a**, however, reduced to 32%, and starting material **1a** was recovered (38%). Portionwise addition of BTC solution to the reaction mixture containing 0.4 equiv of Cp_2TiCl_2 at 0 °C was also found to be fruitless.

Scheme 8



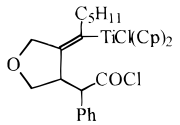
In conclusion, we have found a practical and general bicyclization method of enynes using the Cp_2TiCl_2−Mg−BTC system. The features of this system include a short reaction time, mild reaction conditions, relatively stable starting materials, and good yields, although BTC is still toxic. In addition, this system can be used in the bicyclization of enynes containing a 1,2-disubstituted olefin with highly stereoselectivity. From the viewpoint of elementary reaction, the reaction between BTC and titanacycles is novel and should find use elsewhere. We will investigate the scope of this kind of reaction further.

Experimental Section

General Methods. Melting points are uncorrected. All ^{1}H NMR spectra and ^{13}C NMR spectra are reported in δ units,

(14) Nugent, W. A.; RajanBabu, T. V.; Taber, D. F. *Chem. Scr.* **1989**, *29*, 439.
(15) Urabe, H.; Hata, T.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 4261.
(16) Rajanbabu, T. V.; Nugent, W. A.; Taber, D. F.; Fagan, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7128.

(17) (a) The exact structure like **10** is unknown; however, any other alternatives should keep the retention of stereochemistry from titanacycle to final product in mind. A simliar seven-membered ring intermediate involving a titanium−oxygen bond has also been suggested by Sato. Gao, Y.; Shirai, M.; Sato, F. *Tetrahedron Lett.* **1997**, *38*, 6849. (b) One alternative may be an intermediate like **Y**, which is what we thought in the early stage of this work. However, the stereochemistry outcome of this reaction indicates something contradictory with intermediate **Y**, since an open chain intermediate will most probably fail to give good stereoselectivity.



Y

(18) A catalytic Pauson−Khand reaction is currently available with different metal complexes. For Co, see: (a) Jeong, N.; Hwang, S. H.; Lee, Y.; Chung, Y. K. *J. Am. Chem. Soc.* **1994**, *116*, 3159. (b) Pagenkopf, B.; Livinghouse, T. *J. Am. Chem. Soc.* **1996**, *118*, 2285. For Ru, see: (c) Morimoto, T.; Chatani, N.; Fukumoto, Y.; Murai, S. *J. Org. Chem.* **1997**, *62*, 3762. (d) Kondo, T.; Suzuki, N.; Okada, T.; Mitsudo, T. *J. Am. Chem. Soc.* **1997**, *119*, 6187. For Rh, see: (e) Koga, Y.; Kobayashi, T.; Narasaka, K. *Chem. Lett.* **1998**, 249. For Ti, see ref 6c. An enantioselective catalytic Pauson−Khand- type reaction using titanocene dicarbonyl complex is also known. Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 11688. A catalytic Pauson−Khand reaction in super critical carbon dioxide has been developed. Jeong, N.; Hwang, S. E.; Lee, Y. W.; Lim, J. S. *J. Am. Chem. Soc.* **1997**, *119*, 10549.

parts per million (ppm). Infrared (IR) spectra are reported in wavenumbers (cm^{-1}). Optical rotations were measured on a Perkin-Elmer 241 Autopol Polarimeter. Flash column chromatography was performed on silica gel H (10−40 μM). All cyclization manipulations were performed on a vacuum line using standard Schlenk techniques with a purified argon atmosphere. THF was distilled from sodium/benzophenone ketyl. HMPA was redistilled before use. CH_2Cl_2 was distilled from CaH_2. Cp_2TiCl_2 was prepared according to the literature.[19] Mg powder (Aldrich, 50 mesh) and $P(OEt)_3$ (Fluka, 97%) were used as received. Bis(trichloromethyl) carbonate (BTC) was recrystallized from CH_2Cl_2 and stored in a drybox.

All of the starting enynes and the bicyclization products are colorless oils unless demonstrated otherwise.

The following starting materials were known and thus prepared accordingly: 3-(allyloxy)-1-phenyl-1-propyne[6a] (**1a**), 3-[(2-methyl-2-propenyl)oxy]-1-phenyl-1-propyne[6a] (**1b**), 3-[(3-butenyl)oxy]-1-phenyl-1-propyne[6a] (**1c**), 3-[2(*E*)-butenyl)oxy]-1-phenyl-1-propyne[20] (**1i**), 1-phenyl-6-hepten-1-yne[6a] (**1p**), diethyl 7-octen-2-yne-5,5-dicarboxylate[6a] (**1t**), and diethyl 1-phenyl-6-hepten-1-yne-5,5-dicarboxylate[13] (**1u**). Other starting materials are described below.

General Procedure[21] for Preparation of Starting Enyne Ethers. To a suspension of NaH (80%, 1.32 g, 44 mmol) in 20 mL of dry THF was added dropwise the alcohol (40 mmol) in 10 mL of dry THF. After the mixture was stirred for 20 min at room temperature, the halide (45 mmol) was added portionwise, and the mixture was stirred at ambient temperature for another 1−3 h. The mixture was poured into water, extracted with ether, washed with brine, dried over anhydrous $MgSO_4$, evaporated, and purified by flash chromatography on silica gel (30:1 petroleum ether/ethyl acetate) to give the product.

4-(Allyloxy)-1-phenyl-1-butyne (1d). This material was prepared using the general procedure from 4-phenyl-3-propyn-1-ol[22] and allyl bromide in 96% yield. IR (neat): 2235, 1491 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 7.40 (m, 2H), 7.28 (m, 3H), 5.94 (m, 1H), 5.27 (m, 2H), 4.06 (d, J = 5.5 Hz, 2H), 3.66 (t, J = 7.1 Hz, 2H), 2.71 (t, J = 7.1 Hz, 2H). MS m/z: 186 (M^+, 4.73). HRMS m/z: calcd for $C_{13}H_{14}O$ 186.1045, found: 186.1052.

3-Methyl-3-(allyloxy)-1-phenyl-1-butyne (1e). This material was prepared using the general procedure from 2-methyl-4-phenyl-3-butyn-1-ol[23] and allyl bromide in 36% yield. IR (neat): 2985, 1490 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 7.44 (m, 2H), 7.32 (m, 3H), 6.01 (m, 1H), 5.35 (m, 1H), 5.19 (dd, J = 1.1, 10.3 Hz, 1H), 4.21 (d, J = 5.6 Hz, 2H), 1.60 (s, 6H). MS m/z: 199 ($M^+ - 1$, 0.53). HRMS m/z: calcd for $C_{14}H_{15}O$ $[M - 1]^+$ 199.1123, found 199.1102.

1-(Allyloxy)-1-(2-phenylethynyl)cyclopentane (1f). This material was prepared using the general procedure from 1-(2-phenylethynyl)-cyclopentanol[24] and allyl bromide in 42% yield. IR (neat): 2873, 1599, 1490 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 7.43 (m, 2H), 7.30 (m, 3H), 5.64−6.01 (m, 1H), 5.01−5.36 (m, 2H), 4.16 (m, 2H), 2.09 (m, 4H), 1.70 (m, 4H). MS m/z: 226 (M^+, 1.60). HRMS m/z: calcd for $C_{16}H_{18}O$ 226.1357, found 226.1359.

1-(Allyloxy)-2-octyne (1g). This material was prepared using the general procedure from oct-2-yn-1-ol[25] and allyl bromide in 78% yield. IR (neat): 2958, 1355 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 5.88 (m, 1H), 5.27 (dd, J = 1.5, 17.3 Hz, 1H), 5.17 (dd, J = 0.8, 10.8 Hz, 1H), 4.10 (t, J = 2.1 Hz, 2H), 4.02 (d, J = 5.7 Hz, 2H), 2.18 (m, 2H), 1.48 (m, 2H), 1.30 (m, 4H), 0.87 (t, J = 7.0 Hz, 3H). MS m/z: 166 (M^+, 0.53). HRMS m/z: calcd for $C_{11}H_{17}O$ $[M - 1]^+$ 165.1279, found 165.1283.

(2*R*)-1-(Benzyloxy)-2-[(3-phenyl-2-propyn)oxy]-but-3-ene (1h). This material was prepared using the general procedure from (3*R*)-4-(benzyloxy)-1-but-1-en-3-ol[26] and 1-phenylpropargyl bromide[28] in 80% yield. $[\alpha]^{21}_D$: −49.3° (*c* 1.04, $CHCl_3$). IR (neat): 2238, 1490 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 7.23−7.43 (m, 10H), 5.79 (m, 1H), 5.36 (m, 2H), 4.60 (m, 2H), 4.48 (d, J = 15.7 Hz, 1H), 4.35 (d, J = 15.7 Hz, 1H), 4.27 (m, 1H), 3.58 (m, 2H). δ_C (300 MHz, $CDCl_3$): 56.7, 72.8, 73.4, 78.9, 85.5, 86.1, 119.2, 122.9, 125.9, 127.8, 128.4, 129.0, 131.8, 135.1, 138.3. MS m/z: 292 (M^+, 0.95). HRMS m/z: calcd for $C_{20}H_{20}O_2$ 292.1463, found 292.1468.

1-[(*E*)-Cinnamyloxy]but-2-yne (1k). This material was prepared using the general procedure from but-2-yn-1-ol and cinnamyl bromide[27] in 86% yield. IR (neat): 2850, 2239, 1490 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 7.33 (m, 5H), 6.65 (d, J = 15.9 Hz, 1H), 6.31 (dt, J = 5.9, 15.9 Hz, 1H), 4.24 (m, 2H), 4.17 (q, J = 2.3 Hz, 2H), 0.89 (t, J = 2.3 Hz, 3H). MS m/z: 186 (M^+, 1.02). HRMS m/z: calcd for $C_{13}H_{14}O$ 186.1045, found 186.1025.

1-[(*Z*)-Cinnamyloxy]oct-2-yne (1m). This material was prepared using the general procedure from *Z*-cinnamyl[28] alcohol and 1-bromooct-2-yne[29] in 65% yield. IR (neat): 2933, 1748 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 7.30 (m, 5H), 6.63 (d, J = 11.8 Hz, 1H), 5.87 (dt, J = 6.3, 11.8 Hz, 1H), 4.34 (dd, J = 1.6, 6.4 Hz, 2H), 4.17 (t, J = 2.1 Hz, 2H), 2.19 (m, 2H), 1.49 (m, 2H), 1.33 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H). MS m/z: 242 (M^+, 1.36). HRMS m/z: calcd for $C_{17}H_{22}O$ 242.1671, found 242.1656.

1-[(*E*)-Cinnamyloxy]oct-2-yne (1n). This material was prepared using the general procedure from oct-2-yn-1-ol and cinnamyl bromide in 92% yield. IR (neat): 2933, 2230, 1451 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 7.33 (m, 5H), 6.64 (d, J = 15.9 Hz, 1H), 6.30 (dt, J = 6.1, 15.9 Hz, 1H), 4.23 (dd, J = 0.8, 6.0 Hz, 2H), 4.19 (t, J = 2.1 Hz, 2H), 2.24 (m, 2H), 1.54 (m, 2H), 1.37 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H). MS m/z: 242 (M^+, 0.28). HRMS m/z: calcd for $C_{17}H_{21}O$ $[M - 1]^+$ 241.1593, found 241.1594.

General Procedure[30] for Preparation of Starting Enynes. To a solution of the alkyne (11 mmol) in 15 mL of dry THF and 10 mL of HMPA was added dropwise *n*-BuLi (13 mmol) at −78 °C. The mixture was allowed to reach 0 °C, stirred for 20 min, and then cooled to −30 °C, and the corresponding iodide (12 mmol) was added. After being stirred for an additional 3 h at ambient temperature, the mixture was poured into water, extracted with ether, washed with brine, dried over $MgSO_4$, evaporated, and chromatographed on silica gel (petroleum ether) to give the product.

5,5-Dimethyl-1-phenyl-6-hepten-1-yne (1q). This material was prepared using the general procedure from phenylacetylene and 5-iodo-3,3-dimethyl-1-pentene[31] in 70% yield. IR (neat): 2963, 1491 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 7.40 (m, 2H), 7.29 (m, 3H), 5.79 (dd, J = 10.8, 17.3 Hz, 1H), 4.97 (m, 2H), 2.33 (m, 2H), 1.68 (m, 2H), 1.05 (s, 6H). MS m/z: 198 (M^+, 4.48). HRMS m/z: calcd for $C_{15}H_{18}$ 198.1409, found 198.1417.

9,9-Dimethyl-10-undecen-5-yne (1s). This material was prepared using the general procedure from 1-hexyne and 5-iodo-3,3-dimethyl-1-pentene in 74% yield. IR (neat): 2933, 1641 cm^{-1}. δ_H (300 MHz): 5.72 (dd, J = 10.9, 17.5 Hz, 1H), 4.91 (m, 2H), 2.13 (m, 2H), 2.04 (m, 2H), 1.53 (m, 2H), 1.41 (m, 4H), 0.98 (s, 6H), 0.90 (t, J = 7.0 Hz, 3H). MS m/z: 178 (M^+, 0.09). HRMS m/z: calcd for $C_{12}H_{19}$ $[M - CH_3]^+$ 163.1486, found 163.1485.

General Procedure for the Conversion of Enynes to Bicyclic Cyclopentenones. Typical Procedure A. Under an argon atmosphere, to a solution of 1,2-dibromoethane (50

(19) Siegert, F. W.; Deliefde Merjies, N. J. *J. Organomet. Chem.* **1970**, *23*, 177.
(20) Zhang, M.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 4498.
(21) Brown, C. A.; Barton, D.; Sivaram, S. *Synthesis* **1974**, 434.
(22) Denis, J. N.; Greene, A. E.; Serra, A. A.; Luche, M. J. *J. Org. Chem.* **1986**, *51*, 46.
(23) Yu, W. Y.; Alper, H. *J. Org. Chem.* **1997**, *62*, 5684.
(24) Mayr, H.; Halberstadt-Kausch, I. K. *Chem. Ber.* **1982**, *115*, 3497.
(25) (a) Kanakam, C. C.; Mani, N. S.; Ramanathan, H.; Subba Rao, G. S. R. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1907. (b) Sakai, T.; Hamamoto, H.; Mori, K. *Agric. Biol. Chem.* **1986**, *50*, 1621.
(26) Schnurrenberger, P.; Hungerbühler, E.; Seebach, D. *Liebigs Ann. Chem.* **1987**, 733.
(27) Lin, C.-H.; Aristoff, P. A.; Johnson, P. D.; McGrath, J. P.; Timko, J. M.; Robert, A. *J. Org. Chem.* **1987**, *52*, 5594.
(28) McCombie, S. W.; Nagabhushan, T. L. *Tetrahedron Lett.* **1987**, *28*, 5395.
(29) Crombie, L.; Morgan, D. O.; Smith, E. H. *J. Chem. Soc., Perkin Trans. 1* **1991**, 567.
(30) Beckmann, W.; Doerjer, G.; Logemann, E.; Merkel, C.; Schill, G.; Zürcher, C. *Synthesis* **1975**, 423.
(31) Marshall, J. A.; Cleary, D. G. *J. Org. Chem.* **1986**, *51*, 858.

μL) in dry THF (0.8 mL) was added well-pestled Mg turnings (5 mmol). After being stirred for 15 min, the solvent was removed at reduced pressure, and dry THF (20 mL), Cp_2TiCl_2 (2.2 mmol), the enyne (2 mmol), and $P(OEt)_3$ (4 mmol) were added successively. A solution of BTC (2.5 mmol) in dry THF (5 mL) was added dropwise to the mixture after being stirred at 0 °C for 6 h. (Caution: BTC can slowly generate dangerous phosgene gas.) The mixture was allowed to reach room temperature, stirred for an additional 1−2 h, and then diluted with ether (50 mL), washed with water, dried over $MgSO_4$, concentrated in vacuo, and chromatographed on silica gel (petroleum ether/ethyl acetate) to afford the product.

General Procedure B. Under an argon atmosphere, to a mixture of Cp_2TiCl_2 (2.2 mmol), the enyne (2 mmol), and $P(OEt)_3$ (4 mmol) in dry THF (20 mL) was added Mg powder (2.5 mmol). The mixture was stirred at 0 °C for 6 h. Other operations were the same as procedure A.

The analytical data for the following compounds were identical with those presented in the literature: 2-Phenyl-7-oxabicyclo[3.3.0]oct-1-en-3-one[6a] (**3a**), 3-benzylidene-4-methyltetrahydrofuran[10a] (**4**), 2-phenyl-5-methyl-7-oxabicyclo[3.3.0]-oct-1-en-3-one[6a] (**3b**). 2-phenylbicyclo[3.3.0]oct-1-en-3-one[6a] (**3p**), and diethyl 2-methyl-3-oxobicyclo[3.3.0]oct-1-ene-7,7-dicarboxylate[6a] (**3t**).

(±)-2-Phenyl-8-oxabicyclo[3.4.0]non-1-en-3-one (3c). This compound was prepared using the general procedure A from **1c** in 30% yield. IR (neat): 1702 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 7.20−7.41 (m, 5H), 4.84 (d, J = 13.7 Hz, 1H), 4.28 (d, J = 13.7 Hz, 1H), 4.08 (m, 1H), 3.68 (dt, J = 1.8, 12.0 Hz, 1H), 2.98 (m, 1H), 2.80 (dd, J = 6.5, 18.7 Hz, 1H), 2.24 (dd, J = 3.2, 18.7 Hz, 1H), 2.16 (m, 1H), 1.62−1.76(m, 1H). ^{13}C NMR (300 MHz, $CDCl_3$): 205.7, 169.0, 137.9, 130.1, 129.0, 128.3, 128.2, 67.1, 65.9, 41.6, 37.1, 34.8. MS m/z: 214 (M^+, 70.42). HRMS m/z: calcd for $C_{14}H_{14}O_2$ 214.0993, found 214.1012.

(±)-2-Phenyl-7-oxabicyclo[3.3.0]oct-1-en-3-one (3d). This compound was prepared in the absence of $P(OEt)_3$ using general procedure A from **1d** in 39% yield or procedure B, in 63% yield. IR (neat): 1700 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 7.26−7.43 (m, 5H), 4.35 (m, 1H), 4.20 (m, 1H), 3.39 (dt, J = 2.6, 11.6 Hz, 1H), 3.08−3.20 (m, 2H), 2.92 (d, J = 13.9 Hz, 1H), 2.59−2.77 (m, 2H), 2.05 (d, J = 18.8 Hz, 1H). ^{13}C NMR (300 MHz, $CDCl_3$): 205.2, 172.7, 137.7, 130.6, 129.0, 128.4, 127.9, 126.4, 73.9, 67.8, 39.8, 36.9, 30.6. MS m/z: 214 (M^+, 100). HRMS m/z: calcd for $C_{14}H_{14}O_2$ 214.0993, found 214.1008.

(±)-2-Phenyl-8,8-dimethyl-7-oxabicyclo[3.3.0]oct-1-en-3-one (3e). This compound was prepared using general procedure B from **1e** in 54% yield. Mp: 98−99 °C. IR (neat): 1713 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 7.31 (m, 3H), 7.21 (m, 2H), 4.23 (t, J = 7.5 Hz, 1H), 3.42 (m, 1H), 3.30 (dd, J = 7.8, 11.2.Hz, 1H), 2.71 (dd, J = 6.4, 17.9 Hz, 1H), 2.23 (dd, J = 3.5, 17.9 Hz, 1H), 1.58 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): 207.4, 184.0, 136.1, 130.8, 129.0, 128.3, 78.7, 69.9, 43.9, 39.2, 29.2, 24.1. MS m/z: 228 (M^+, 19.32). HRMS m/z: calcd for $C_{15}H_{16}O_2$ 228.1550, found 228.1550.

(±)-6-Phenyl-3a,4-dihydrospiro(1*H*-cyclopenta[c]furan-1,1′-cyclopentan)-5(3*H*)-one (3f). This compound was prepared using the general procedure A from **1f** in 43% yield or procedure B in 78% yield. Mp: 93−94 °C. IR (KBr): 1701 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 7.38 (m, 3H), 7.27 (m, 2H), 4.30 (t, J = 7.7 Hz, 1H), 3.48 (m, 1H), 3.29 (dd, J = 7.9, 11.2 Hz, 1H), 2.78 (dd, J = 6.4, 17.8 Hz, 1H), 2.31 (dd, J = 3.7, 17.8 Hz, 1H), 2.21 (m, 2H), 1.88 (m, 1H), 1.69 (m, 2H) 1.55 (m, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): 207.5, 183.7, 135.8, 132.0, 131.0, 129.3, 128.4, 89.0, 69.9, 45.1, 41.4, 39.4, 36.2, 25.2. MS m/z: 254 (M^+, 100). HRMS m/z: calcd for $C_{17}H_{18}O_2$ 254.1306, found 254.1303.

(±)-2-*n*-Pentyl-7-oxabicyclo[3.3.0]oct-1-en-3-one (3g). This compound was prepared using the general procedure A from 1g in 41% yield or procedure B in 77% yield. IR (neat): 1712 cm^{-1}. δ_H (300 MHz $CDCl_3$): 4.61 (d, J = 15.5 Hz, 1H), 4.51 (d, J = 15.6 Hz, 1H), 4.31 (m, 1H), 3.18 (m, 2H), 2.66 (dd, J = 5.6, 17.6 Hz, 1H), 2.07−2.30 (m, 3H), 1.21−1.49 (m, 6H), 0.88 (t, J = 7 Hz, 3H). ^{13}C NMR (300 MHz $CDCl_3$): 209.1, 176.0, 137.0, 72.2, 64.8, 43.3, 39.1, 31.5, 27.3, 24.1, 22.2, 13.9. MS m/z: 195 (M^+ + 1, 100). HRMS m/z: calcd for $C_{12}H_{18}O_2$ 194.1306, found 194.1291

(−)-(5*S*,5α,6*β*)-2-Phenyl-6-(benzyloxymethyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one (3h). This compound was prepared using general procedure A from **1h** in 45% yield or procedure B in 64% yield. $[\alpha]^{20}_D$: −63.3° (c 1.25, $CHCl_3$). IR (neat): 1709 cm^{-1}. δ_H (300 MHz $CDCl_3$): 7.51 (m, 2H), 7.32−7.44 (m, 8H), 5.04 (dd, J = 1.4, 16.2 Hz, 1H), 4.67 (dt, J = 1.3, 16.2 Hz, 1H), 4.64 (s, 2H), 3.76 (m, 2H), 3.64 (dt, J = 4.5, 10.3 Hz, 1H), 3.17 (m, 1H), 2.79 (ddd, J = 0.4, 6.5, 17.8 Hz, 1H), 2.35 (dd, J = 3.5, 17.8 Hz, 1H). ^{13}C NMR (300 MHz $CDCl_3$): 206.7, 177.2, 137.9, 135.0, 130.5, 128.7, 128.5, 128.3, 128.1, 127.9, 127.7, 81.7, 73.7, 70.7, 67.0, 45.3, 40.2. MS m/z: 321 (M^+ + 1, 59.86). HRMS m/z: calcd for $C_{21}H_{20}O_3$ 320.1413, found 320.1418.

(±)-(4α,5α)-4-Methyl-2-phenyl-7-oxabicyclo[3.3.0]oct-1-en-3-one (3i). This compound was prepared using the general procedure B from **1i** in 63% yield. IR (neat): 1709 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 7.53 (m, 2H), 7.35 (m, 3H), 4.93 (dd, J = 1.6, 16.6 Hz, 1H), 4.61 (dd, J = 0.5, 16.4 Hz, 1H), 4.42 (t, J = 8.0 Hz, 1H), 3.29 (dd, J = 8.0, 11.1 Hz, 1H), 2.98 (m, 1H), 2.35 (dq, J = 4.0, 7.2 Hz, 1H), 1.35 (d, J = 7.2 Hz, 3H). ^{13}C NMR (300 MHz $CDCl_3$): 208.8, 174.7, 133.8, 130.9, 128.7, 128.6, 128.0, 71.2, 66.5, 52.1, 47.5, 13.8. MS m/z: 214 (M^+, 85.48). HRMS m/z: calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0991.

(±)-(4α,5α)-2-Methyl-4-phenyl-7-oxabicyclo[3.3.0]oct-1-en-3-one (3k). This compound was prepared using the general procedure A from **1k** in 32% yield. IR (neat): 1718 cm^{-1}. δ_H (400 MHz, $CDCl_3$): 7.16−7.35 (m, 5H), 4.64 (d, J = 15.7 Hz, 1H), 4.54 (d, J = 15.7 Hz, 1H), 4.37 (t, J = 5.8 Hz, 1H), 3.32−3.40 (m, 2H), 3.29 (d, J = 3.4 Hz, 1H), 1.83 (s, 3H). ^{13}C NMR (400 MHz $CDCl_3$): 208.2, 174.0, 137.8, 131.4, 128.8, 128.3, 127.2, 71.7, 64.9, 57.0, 52.3, 9.4. MS m/z: 214 (M^+, 52.88). HRMS m/z: calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0990.

(±)−(4α,5*β*)-2-Pentyl-4-phenyl-7-oxabicyclo[3.3.0]oct-1-en-3-one (3m). This compound was prepared using the general procedure B from **1m** in 74% yield. IR (neat): 1714 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 7.24 (m, 3H), 6.95 (m, 2H), 4.64 (d, J = 15.8 Hz, 1H), 4.54 (dd, J = 0.8, 15.8 Hz, 1H), 4.00 (d, J = 7.2 Hz, 1H), 3.86 (t, J = 8.2 Hz, 1H), 3.53 (m, 1H), 2.84 (dd, J = 8.3, 11.3 Hz, 1H), 2.33 (m, 2H), 1.54 (m, 2H), 1.34 (m, 4H), 0.91 (t, J = 6.8 Hz, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): 209.4, 176.1, 137.0, 128.7, 128.2, 127.1, 68.2, 65.5, 54.1, 48.9, 31.8, 27.4, 24.3, 22.4, 14.0. MS m/z: 270 (M^+, 100). HRMS m/z: calcd for $C_{18}H_{22}O_2$ 270.1620, found 270.1619.

(±)-(4α,5α)-2-Pentyl-4-phenyl-7-oxabicyclo[3.3.0]oct-1-en-3-one (3n). This compound was prepared using the general procedure B from **1n** in 61% yield. IR (neat): 1717 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 7.17−7.38 (m, 5H), 4.68 (d, J = 15.7 Hz, 1H), 4.58 (d, J = 15.7 Hz, 1H), 4.38 (m, 1H), 3.37 (m, 3H), 2.31 (m, 1H), 2.22 (m, 1H), 1.51 (m, 2H), 1.32 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): 208.0, 173.5, 137.9, 135.9, 128.9, 128.6, 128.5, 128.3, 127.3, 71.8, 65.2, 57.2, 52.5, 31.8, 27.5, 24.6, 22.5, 14.0. MS m/z: 270 (M^+, 100). HRMS m/z: calcd for $C_{18}H_{22}O_2$ 270.1620, found 270.1649.

(±)-6,6-Dimethyl-2-phenylbicyclo[3.3.0]oct-1-en-3-one (3q). This compound was prepared using the general procedure A from **1q** in 70% yield. IR (neat): 1701 cm^{-1}. δ_H (300 MHz $CDCl_3$): 7.62 (m, 2H), 7.40 (m, 2H), 7.29 (m, 1H), 2.94 (dd, J = 10.4, 19.5 Hz, 1H), 2.81 (m, 1H), 2.67 (m, 1H), 2.55 (dd, J = 6.5, 18.0 Hz, 1H), 2.25 (dd, J = 3.2, 18.1 Hz, 1H), 1.95 (m, 1H), 1.81 (m, 1H), 1.19 (s, 3H), 0.67 (s, 3H). ^{13}C NMR (300 MHz $CDCl_3$): 208.7, 184.9, 134.9, 131.8, 128.3, 128.2, 127.7, 54.7, 41.4, 38.6, 37.4, 27.7, 26.9, 20.2. MS m/z: 226 (M^+, 100). HRMS m/z: calcd for $C_{16}H_{18}O$ 226.1358, found 226.1354.

(±)-2-Butyl-6,6-dimethylbicyclo[3.3.0]oct-1-en-3-one (3s). This compound was prepared using the general procedure B from **1s** in 58% yield. IR (neat): 1706 cm^{-1}. δ_H (300 MHz $CDCl_3$): 2.59 (m, 1H), 2.49 (m, 2H), 2.31 (dd, J = 6.3, 18.1 Hz, 1H), 2.11 (m, 2H), 1.98 (dd, J = 3.0, 18.1 Hz, 1H), 1.78 (m, 2H), 1.36 (m, 2H), 1.23 (dd, J = 7.2, 15.1 Hz, 2H), 1.10 (s, 3H), 0.84 (t, J = 7.2 Hz, 3H), 0.59 (s, 3H). ^{13}C NMR (300 MHz $CDCl_3$): 210.9, 183.4, 136.9, 54.5, 41.4, 38.7, 36.4, 30.1, 27.8, 24.7, 23.4, 22.7, 20.0, 13.9. MS m/z: 206 (M^+, 80.72). HRMS m/z: calcd for $C_{14}H_{22}O$ 206.1670, found 206.1676.

(±)-Diethyl 2-phenyl-3-oxobicyclo[3.3.0]oct-1-ene-7,7-dicarboxylate (3u). This compound was prepared using the general procedure A from **1u** in 46% yield or Procedure B in 65% yield. IR (neat): 1732, 1707 cm^{-1}. δ_H (300 MHz): 7.24−7.57 (m, 2H), 7.38 (m, 3H), 4.28 (q, J = 7.1 Hz, 2H), 4.17 (dq, J = 2.5, 7.1 Hz, 2H), 3.64 (d, J = 19.2 Hz, 1H), 3.29 (d, J = 19.2 Hz, 1H), 3.12 (m, 1H), 2.82 (m, 2H), 2.31 (dd, J = 3.3, 17.8 Hz, 1H), 1.76 (t, J = 12.6 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): 207.1, 179.0, 171.6, 170.7, 135.6, 131.0, 128.5, 128.2, 62.2, 62.0, 61.4, 42.9, 42.7, 38.8, 36.0, 14.1, 14.0. *m*/*z* (%): 342 (M^+, 31.77), 268 (100). HRMS *m*/*z*: calcd for $C_{20}H_{22}O_5$ 342.1467, found 342.1467.

Bicyclic Titanacycle (2m). Under an argon atmosphere, to a mixture of Cp_2TiCl_2 (2.2 mmol), enyne **1m** (2 mmol), and $P(OEt)_3$ (4 mmol) in dry THF (20 mL) was added Mg powder (2.5 mmol). The mixture was stirred at 0 °C for 6 h and then passed through a short silica gel plug eluting with dry CH_2Cl_2. The solvents were removed under reduced pressure, and the black residue was chromatographed on silica gel (15:1 petroleum/CH_2Cl_2) to give 560 mg (66%) of a dark-purple viscous material. An analytical sample was obtained by further purification by flash chromatography on silica gel. IR (neat): 3024, 2957, 2927, 2856, 1595, 1489, 1446, 1048, 1019, 918, 813, 752, 697 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 7.14 (m, 2H), 6.83 (m, 3H), 6.23 (s, 5H), 5.81 (s, 5H), 4.29 (d, J = 12.6 Hz, 1H), 4.19 (t, J = 7.1 Hz, 1H), 3.93 (d, J = 12.6 Hz, 1H), 3.73 (d, J = 10.2 Hz, 1H), 2.86 (m, 1H), 2.73 (dd, J = 7.7, 10.2 Hz, 1H), 2.15 (m, 1H), 2.05 (m, 1H), 1.0−1.35 (m, 6H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): 194.4, 152.3, 128.5, 128.1, 126.5, 123.5, 121.2, 119.8, 113.9, 113.4, 78.1, 70.5, 63.8, 40.6, 38.7, 32.6, 29.6, 22.6, 14.1. MS (FAB): 420 (M^+). Anal. Calcd for $C_{27}H_{32}OTi$: C, 77.14, H, 7.66. Found: C, 76.90, H, 7.92.

Acknowledgment. We thank the National Natural Science Foundation for support of this research.

Supporting Information Available: ^1H NMR spectra for new compounds **1d**−**g**,**k**,**m**,**n**,**q**,**s**, **2m**, and **3c**−**i**,**k**,**m**,**n**,**q**,**s**,**u** (23 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9810718